

PTO 08-2904

CC=WO DATE=20000615 KIND=A2  
PN=0035259

METHOD FOR PRODUCING PRINTED CONDUCTOR STRUCTURES  
[Verfahren zur Herstellung von Leiterbahnstrukturen]

G. Naundorf, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. March 2008

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	WO
DOCUMENT NUMBER	(11):	00/35259
DOCUMENT KIND	(12):	A2
PUBLICATION DATE	(43):	20000615
APPLICATION NUMBER	(21):	PCT/DE99/03965
APPLICATION DATE	(22):	19991210
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	H05K 3/00
PRIORITY	(30):	Dec 10, 1998[DE] 19856888.6
INVENTOR	(72):	Naundorf, G.; Wissbrock, H.
APPLICANT	(71):	Naundorf, G.; Wissbrock, H.
TITLE	(54):	METHOD FOR PRODUCING PRINTED CONDUCTOR STRUCTURES
FOREIGN TITLE	[54A]:	VARIABLE

This invention relates to a method for producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied on the substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structures being produced, heavy metal seeds being released and metallizing said region by chemical reduction. /1\*

From the offprint "LAD - Ein neuartiges lasergestütztes Beschichtungsverfahren für Feinstleitermetallisierungen" [LAD: A Novel Laser-Assisted Coating Process for the Finest Conductor Metallization] from No. 10, Vol. 81 (1990) of Fachzeitschrift "Galvanotechnik", it is known, for producing fine conductor structures of well under 100  $\mu\text{m}$  on a nonconductive substrate material, to apply Pd-acetate from solution over the entire surface, in the form of a thin film. Then, by subsequent laser radiation using an excimer laser with a wavelength of 248 nm, metal atoms are intended to be released as seeds for subsequent currentless metallization in the region of the conductor structures that are being produced. However, before metallization a rinsing process must be carried out to remove the undecomposed regions of the metal-containing film that has been applied to the substrate material. The quality of this

---

\* Number in the margin indicates pagination in the foreign text.

rinsing process plays a crucial role in avoiding wild growth problems during the subsequent currentless metallization. It has also been found that the process just described does not provide sufficient adhesive strength on the part of the deposited metallic conductive paths.

DE 42 10 400 C1 describes a method for direct deposition of copper from a film applied to a substrate from a mixture of heavy metal salts, by local heating by a laser. This method is in the field of thermally activated chemistry and has the disadvantage that the fineness of the conductor structures that can be achieved is limited. Moreover, the film that is applied is an electrically conductive film, so that a difficult and expensive rinsing process is required before metallization. The use of a nonconductive heavy metal complex and cold breakup of the heavy metal complex with UV laser radiation for splitting off the heavy metal seeds is clearly suggested here. /2

US 45 74 095 makes known a method in which a substrate in a vacuum chamber is subjected to the vapor of a palladium complex and then structured using radiation from a 249 nm excimer laser through a window. Since the palladium deposition occurs from a vapor phase in a vacuum chamber, this method is so expensive that its use in conventional circuit boards and substrates is not economical.

The object of the present invention is to create a simplified and reliable process for producing conductor structures that will

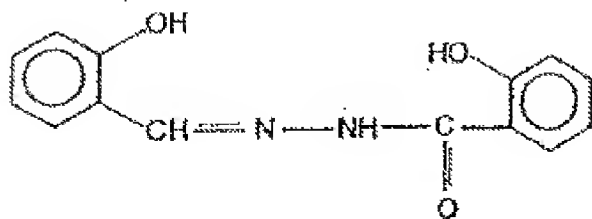
reliably provide extremely fine structuring of the conductive paths, down to conductive path widths and spacings of 10  $\mu\text{m}$ .

This object is achieved by the characteristics of Claims 1 through 13. The additional design of the invention may be found in the dependent claims.

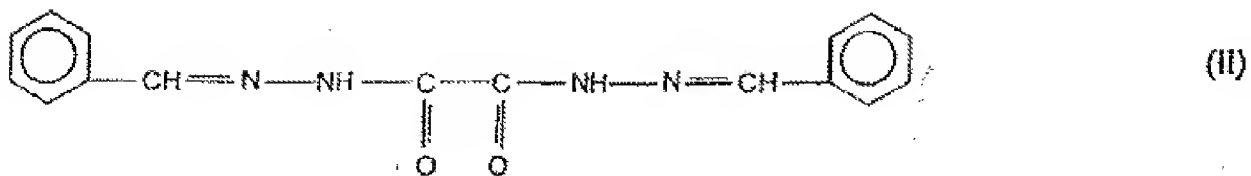
Within the scope of the invention, it is envisaged that the heavy metal complex is formed with organic complexing agents having the chemical structures of carboxylic acid amides of aliphatic and aromatic mono- and dicarboxylic acids and their N-monosubstituted derivatives, such as N, N'-diphenyloxalic acid diamide.

Moreover, it is envisaged that the heavy metal complex is formed with organic complexing agents having chemical structures of cyclic amides, such as barbituric acid.

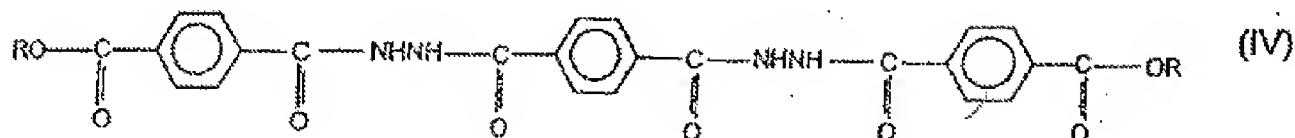
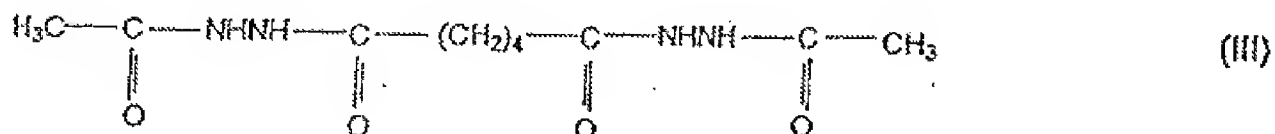
It is also possible to form the heavy metal complex using organic complexing agents having chemical structures of hydrazones (I) and bishydrazones (II) of aliphatic and preferably aromatic aldehydes, such as benzaldehyde and salicylaldehyde or of o-hydroxy aryl ketones.



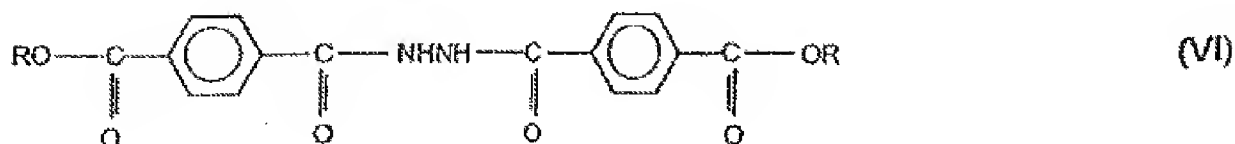
(I)



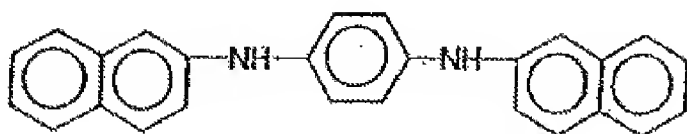
Alternatively, it is possible for the heavy metal complex to be formed with organic complexing agents having chemical structures of hydrazides of aliphatic and aromatic mono- and dicarboxylic acids and their N-acylated derivatives, such as (III) and (IV).



Within the scope of this invention, it is envisaged that the heavy metal complex can also be formed with organic complexing agents having chemical structures of diacylated hydrazines, such as (V) and (VI).

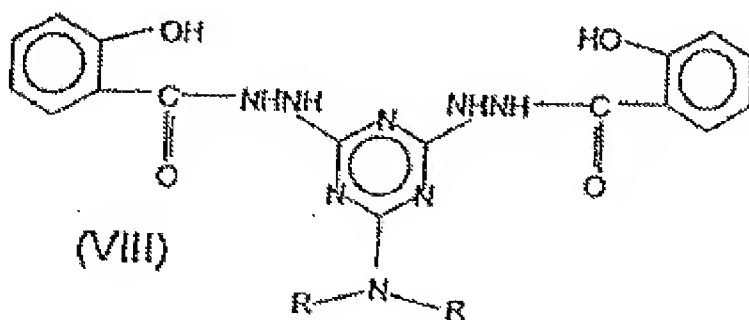


Moreover, it is possible for the heavy metal complex to be formed with organic complexing agents having chemical structures of phenylenediamines, such as N, N'-di-2-naphthyl-p-phenylenediamine (VII).

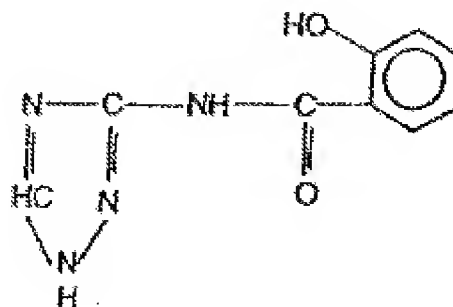


(VII)

It has been found that it is also possible for the heavy metal complex to be formed with organic complexing agents having chemical structures of heterocyclic compounds, such as melamine derivatives, benzotriazoles, 8-oxyquinoline, hydrazones, and acylated derivatives of hydrazinotriazines, such as (VIII), aminotriazoles and their acylated derivatives, such as (IX).

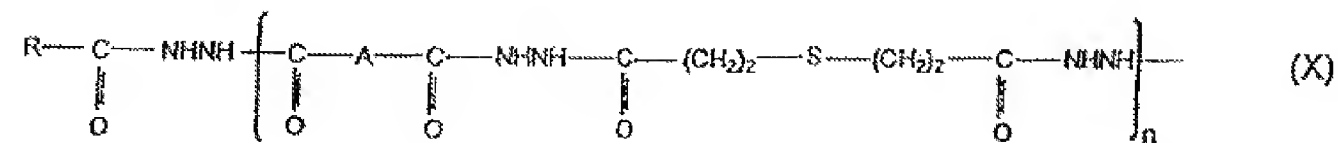


(VIII)

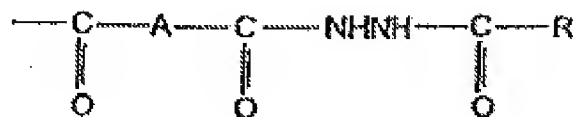


(IX)

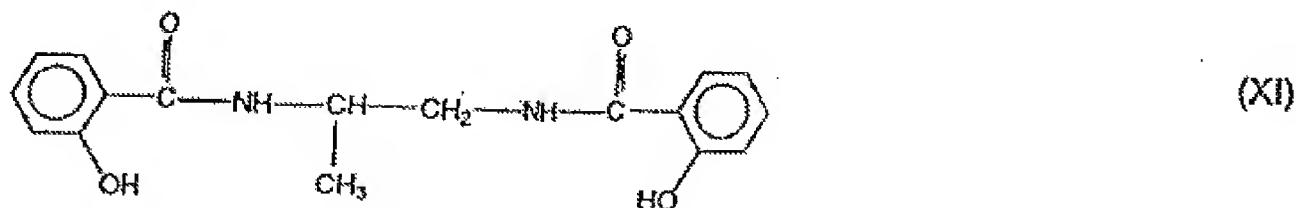
Alternatively, it is also possible for the heavy metal complex with organic complexing agents with chemical structures of polyhydrazides, such as (X).



$n = 1$  to  $10$ ,  $\text{A} =$  alkylene or phenylene

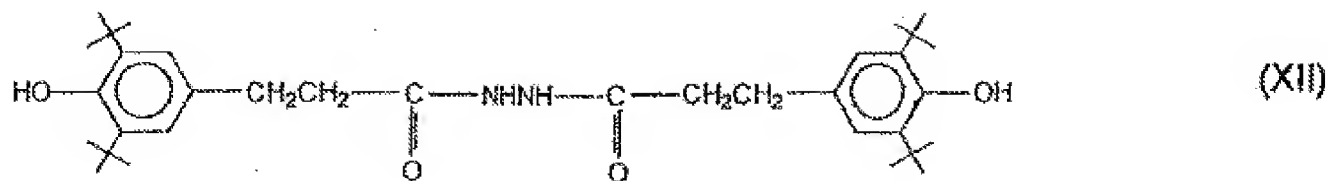


It is also envisaged that the heavy metal complex is formed /5  
with organic complexing agents having chemical structures of disalicylidenes, such as N, N'-disalicylidene 1,2-diaminopropane (XI)

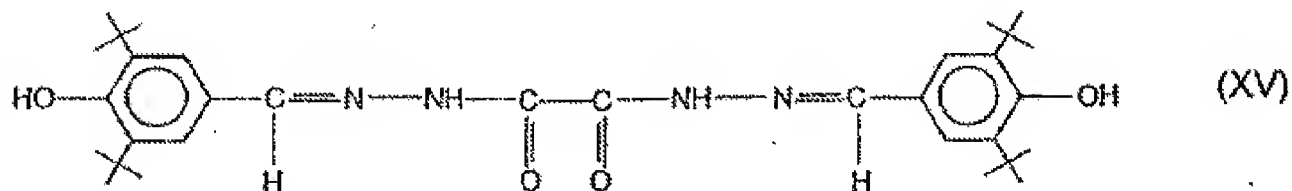
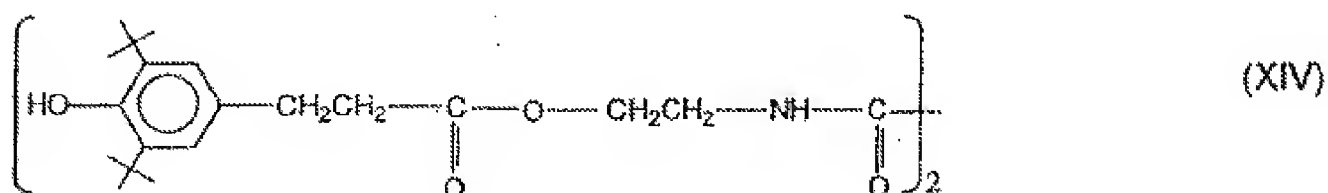
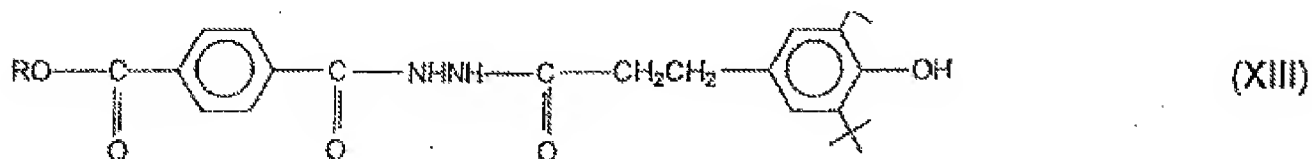


Moreover, it is envisaged that the heavy metal complex is formed with organic complexing agents having chemical structures of molecular combinations of sterically hindered phenols and metal-complexing groups, such as (XII), (XIII), (XIV and (XV).

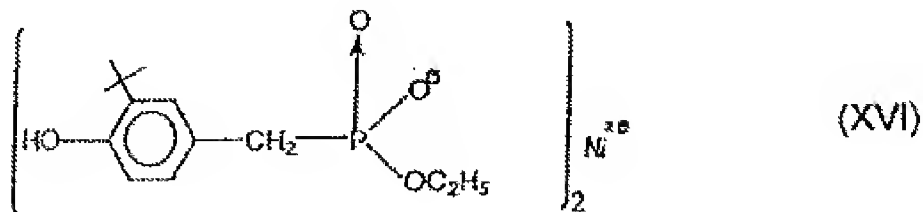




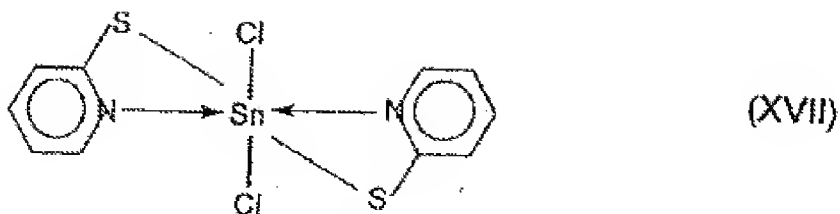
(+ = tert-butyl group)



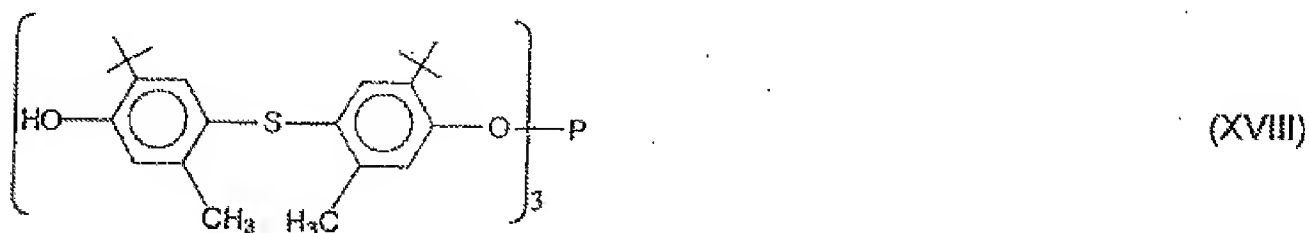
Alternatively, it is also envisaged that the heavy metal complex is formed with organic complexing agents having chemical structures of benzylphosphoric acid Ni salts, such as (XVI), alone or in combination with other complexing agents mentioned here.



Moreover, it can be envisaged that the heavy metal complex is formed with organic complexing agents having chemical structures of pyridinethiol Sn compounds, such as (XVII)



Within the scope of the invention, it is also envisaged that the heavy metal complex is formed with organic complexing agents having chemical structures of tert-phosphorous acid esters of a sulfur-containing bisphenol, such as (XVIII).



The above-mentioned complexing agents possess the advantageous property that they are sufficiently soluble or easily dispersible in polymer phases and are also highly compatible. Due to their good compatibility, harmful blooming properties can be avoided.

The above-mentioned complexing agents are also highly /7  
extraction-resistant and durable in alkaline and acidic chemical and galvanic baths. These complexing agents are also advantageously unvolatile and not acutely toxic, nor are they irritating to the skin or mucous membrane.

The heavy metal complexes formed by reacting the above-mentioned organic complexing agents with heavy metal salts are characterized in that they are temperature-resistant and their decomposition

temperature is above the injection molding temperature of thermoplastic materials and the curing temperature of the coating. Moreover, the temperature effects during the soldering process cannot trigger decomposition of the heavy metal complexes used in accordance with this invention. Thus, the heavy metal complexes also remain nonconductive in the vicinity of the conductive paths.

Since nonconductive organic heavy metal complexes are used as the heavy metal-containing component, which are formed by reaction of heavy metal salts with organic complexing agents and the heavy metal seeds are split off by means of UV radiation, by breaking up the heavy metal complexes in the region of the conductive paths, the result is that the chemically reductive metallization can occur immediately following the effects of the UV radiation. Due to the effects of the UV radiation, a breakup of the heavy metal complexes in the region of the conductor structures being produced, highly reactive heavy metal seeds are split off for the partial reductive metallization. The metallization occurs with no wild growth, forming very sharp contours. Since the heavy metal seeds that are formed are highly reactive, the desired exact metallization in the required layer thickness is also promoted. Since the substrate material has a microporous surface, excellent adhesive strength of the deposited metallic conductive paths is also achieved.

It is envisaged in accordance with this invention that the heavy metal complexes are dissolved in a solvent, e.g., dimethylformamide,

and applied to a porous substrate material or on a substrate material with a porous surface. This may be, for example, a flexible polyimide membrane film with a microporous surface or paper. In this case, the heavy metal complex can penetrate into the pores of the material. In the subsequent metallization, the pore structure is advantageous for the adhesion of the conductive track, into which the copper, which is used by way of example for the metallization, grows and clings there in the manner of a root. The very fine structures that can be /8 achieved are promoted in that no adhesion-agent layer is required and, as a result, no lower limit of possible conductive path widths is given. In addition, because of its short wavelength, the UV radiation used here makes possible extremely sharp structures with metallization seeds.

Alternatively, it is envisaged that the substrate material is made of microporous or microrough carrier particles, the carrier particles are mixed into the substrate material and/or applied to the substrate material and bound there, the electromagnetic UV radiation is selectively applied to the substrate material in the region of the conductor structures being produced, in such a way that carrier particles are exposed by removal and then, by breaking up of the bound heavy metal complexes, the heavy metal seeds are released and this region is then metallized by chemical reduction to form the conductor structures.

In a preferred embodiment of the invention, palladium salts are used as the heavy metal salts. Alternatively, the palladium salts can also be used in conjunction with the salts of other heavy metals. It can also be advantageous if a palladium acetate is used as the heavy metal salt. Pd complexes or Pd-containing heavy metal complexes are advantageously used. It has been found that such heavy metal complexes are particularly well suited for extremely fine structuring in accordance with this method of this invention. In particular, for initiating the structuring cleavage reaction, UV radiation requires far less energy density than removal using known systems. Another achievement is that, in conjunction with the structuring, for each laser pulse of an excimer laser a much greater surface area can be exposed than with known ablation techniques.

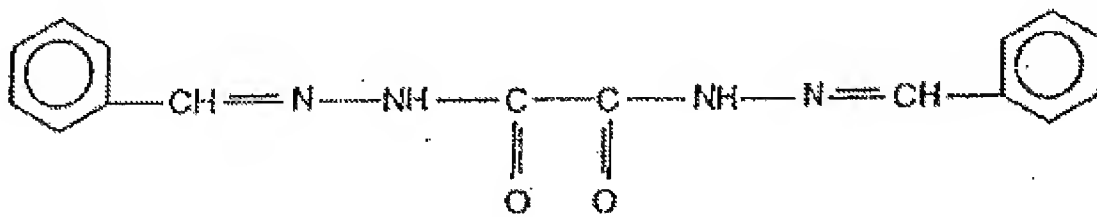
It is also envisaged within the scope of the invention that for splitting of the heavy metal seeds from the heavy metal complex, a KrF excimer laser with a wavelength of 248.5 nm or a frequency tripler Nd:YAG laser with a wavelength of 355 nm is preferably used. In this way, the split can be performed without heating the complex. This prevents melting of the material in the affected region. The result is a very high boundary sharpness in the region with the split-off heavy metal seeds and the resulting very high, extremely advantageous edge sharpness on the part of the metal structures, which is of particularly great importance in very fine conductors.

/9

The method in accordance with this invention can be applied with full-surface laser radiation and masking techniques in efficient mass production and in maskless, point-focused laser beam applications using, for example, NC technology.

The invention will be explained below with the help of an exemplary embodiment:

2.24 parts by mass palladium diacetate is dissolved in 100 parts by mass dimethylformamide. 2.94 parts by mass organic complexing agent of the formula



are also placed in 800 parts by mass dimethylformamide and dissolved by heating. The two solutions are then mixed and allowed to react. Immediately afterward, before the solution has cooled and the resulting palladium complex has precipitated, a microporous polyimide film is saturated in the solution. After 10 hours of drying at room temperature, the base material prepared in this way is irradiated using a mask with a KrF excimer laser, i.e., an excimer laser having a wavelength of 248.5 nm. In the irradiated regions, very finely divided metallic palladium is split out of the complex. In a commercially available reductive, copper bath with no external current, strongly adhering, anchored copper is selectively deposited

in the irradiated regions. The conductors are formed and finished, flexible circuit results.

It has been found that the inventive process can also be used to apply conductor structures on substrates made of other nonconductive materials with microporous surfaces, such as ceramic base materials or glass.

It is also within the scope of the invention for heavy metal complexes to be incorporated into the substrate material, e.g., into a thermoplastic. The action of the UV laser radiation on the /10 surface of the injection molding part in the region of the conductive paths being applied then causes ablation of the substrate material, breaking up the released heavy metal complexes, so that heavy metal seeds are split off, which make possible currentless metallization to form the conductive paths.

1. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of carboxylic acid amides of aliphatic and aromatic mono- and dicarboxylic acids and their N-monosubstituted derivatives.

2. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material, the substrate material is selectively subjected to UV laser radiation in the region of the conductor structures being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of cyclic amides.

3. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an



electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of hydrazones and bishydrazones of aliphatic and preferably aromatic aldehydes.

4. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and /12 the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of hydrazides of aliphatic and aromatic mono- and dicarboxylic acids and their N-acylated derivatives.

5. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the

substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of diacylated hydrazine.

6. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of phenylenediamine.

7. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed

with organic complexing agents having chemical structures of heterocyclic compounds, such as melamine derivatives, benzotriazoles, 8-oxyquinoline, hydrazones, and the acylated derivatives of hydrazinotriazines.

8. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of polyhydrazides.

/13

9. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of disalicylidenes.

10. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of molecular combinations of sterically hindered phenols and metal-complexing groups.

11. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of benzylphosphoric acid-Ni salts.

12. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said

/14

substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of pyridinethiol-Sn compounds.

13. A method of producing fine metallic conductor structures on an electrically nonconductive substrate material, wherein an electrically nonconductive heavy metal complex is applied to said substrate material or introduced into the substrate material and the substrate material is selectively subjected to UV laser radiation in the region of the conductor structure being produced, heavy metal seeds being released and moralizing said region by chemical reduction, characterized in that the heavy metal complex is formed with organic complexing agents having chemical structures of tert-phosphorous acid esters of a sulfurous bisphenol.

14. A method as recited in one of the Claims 1 through 13, characterized in that a Pd heavy metal complex formed by reacting an organic complexing agent with a palladium salt is applied or introduced.

15. A method as recited in one of the Claims 1 through 13, characterized in that a Pd-containing heavy metal complex is applied or introduced.

16. A method as recited in Claim 15, characterized in that the Pd-containing heavy metal complex is formed by reacting a palladium salt in conjunction with salts of other heavy metals.

17. A method as recited in Claims 14 and 16, characterized in that a palladium diacetate is used as the palladium salt.